

## Convective dissolution of carbon dioxide in saline aquifers

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[1] Geological carbon dioxide (CO<sub>2</sub>) storage is a means of reducing anthropogenic emissions. Dissolution of CO<sub>2</sub> into the brine, resulting in stable stratification, increases storage security. The dissolution rate is determined by convection in the brine driven by the increase of brine density with CO<sub>2</sub> saturation. We present a new analogue fluid system that reproduces the convective behaviour of CO<sub>2</sub>-enriched brine. Laboratory experiments and high-resolution numerical simulations show that the convective flux scales with the Rayleigh number to the 4/5 power, in contrast with a classical linear relationship. A scaling argument for the convective flux incorporating lateral diffusion from downwelling plumes explains this nonlinear relationship for the convective flux, provides a physical picture of high Rayleigh number convection in a porous medium, and predicts the CO<sub>2</sub> dissolution rates in CO<sub>2</sub> accumulations. These estimates of the dissolution rate show that convective dissolution can play an important role in enhancing storage security.

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[2] The storage of carbon dioxide (CO<sub>2</sub>) in geological formations has been proposed as a technological means to reduce anthropogenic emissions of this greenhouse gas [Orr, 2009; Benson and Cook, 2006]. The positive buoyancy of supercritical CO<sub>2</sub> relative to the ambient brine filling the pore spaces may lead to leakage along imperfections in the geological seal, which is of considerable concern for the security of long-term storage [Gasda et al., 2004; Pruess, 2005; Neufeld et al., 2009]. One of the primary mechanisms for stable long-term geological storage of CO<sub>2</sub> is the dissolution of injected CO<sub>2</sub> within ambient brine. Under typical conditions injected CO<sub>2</sub> dissolves into the ambient brine thereby increasing the density of the brine [Teng et al., 1997]. This layer of dense, saturated brine forms by the processes of diffusion, dispersion and mechanical mixing during injection and, once it has reached sufficient thickness, becomes rapidly unstable to convective overturning [Ennis-King et al., 2005; Riaz et al., 2006]. The process of convective dissolution of

CO<sub>2</sub> has recently been imaged at ambient conditions in a Hele-Shaw cell [Kneafsey and Pruess, 2009], and enhanced mass transfer has been measured at reservoir conditions [Yang and Gu, 2006; Farajzadeh et al., 2007]. Convection is therefore expected in most sequestration sites, and controls the dissolution rate and hence the long-term risk of leakage. Geochemical observations in natural CO<sub>2</sub> reservoirs require large amounts of CO<sub>2</sub> dissolution into the ambient brine and provide field evidence for sustained convective transport of dissolved CO<sub>2</sub> [Gilfillan et al., 2008, 2009]. Convective dissolution of CO<sub>2</sub> is therefore expected in most natural and anthropogenic CO<sub>2</sub> reservoirs, and controls the mobility of carbon in the subsurface. It is therefore an important mechanism in the deep carbon cycle [Sherwood and Ballentine, 2009], and controls the long-term risk of leakage of CO<sub>2</sub> from geological storage.

[3] Despite the recognized importance of convective dissolution in geological CO<sub>2</sub> reservoirs, no systematic experimental or numerical data set constrains the convective flux as a function of average reservoir properties. This lack of data is due to the difficulty of conducting large experiments at reservoir conditions [Kneafsey and Pruess, 2009; Yang and Gu, 2006; Farajzadeh et al., 2007] and the high resolution required for numerical simulations [Riaz et al., 2006; Lu and Lichtner, 2007; Pau et al., 2010; Otero et al., 2004]. To overcome these limitations we explore a novel analogue fluid system that allows quantitative measurement of the convective flux using a combination of laboratory experiments and high-order numerical simulations (see auxiliary material).<sup>1</sup>

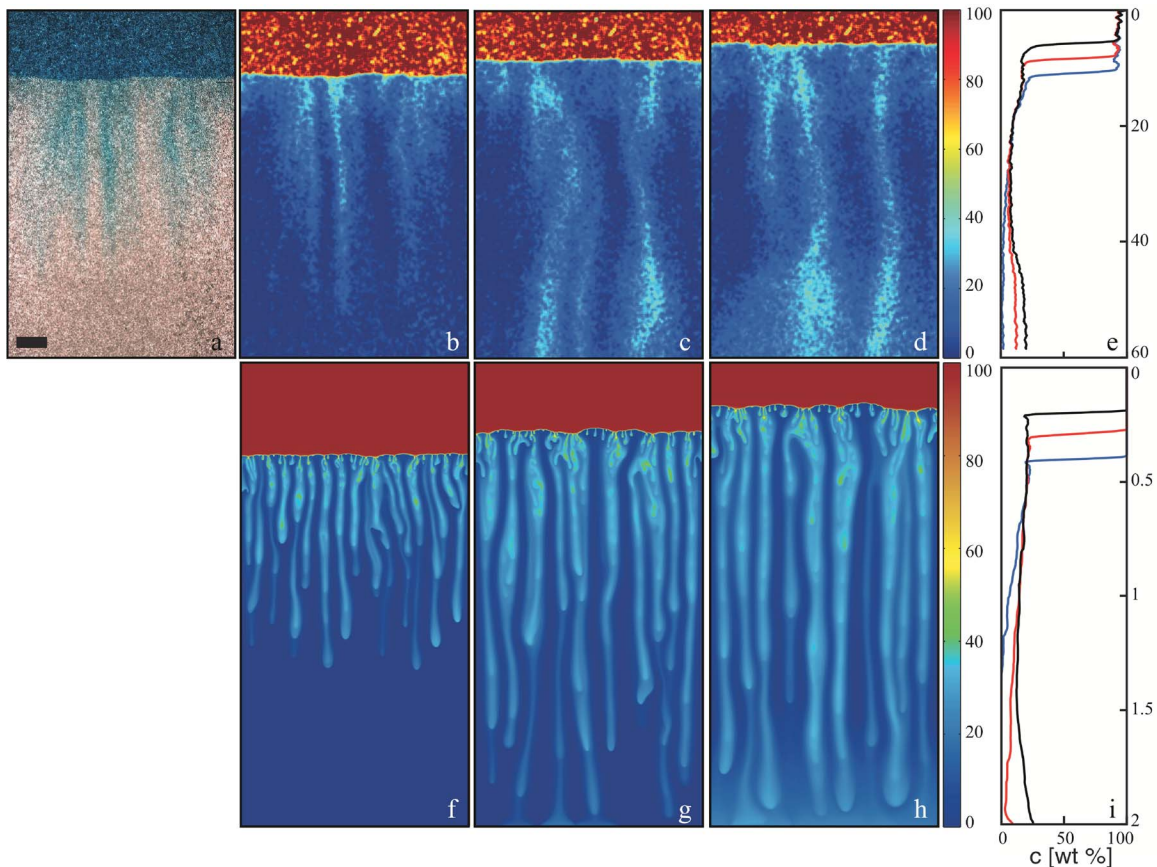
[4] We have developed a new experimental analogue that models convective dissolution of CO<sub>2</sub> using solutions of methanol and ethylene-glycol (MEG) mixing with water [Huppert et al., 1986] as shown in (Figures 1a–1d). MEG solutions containing less than 68 wt% ethylene-glycol are less dense than water, but the density of MEG-water mixtures may exceed that of water, with a maximum between 30 and 50 wt% MEG, dependent on the ethylene-glycol content of the MEG (Figure 2). The mixing of a buoyant layer of MEG at the top of a deep reservoir of water therefore mimics the dissolution of CO<sub>2</sub> into brine, as mixing of MEG with water leads to an increase in density resulting in convective motions (Figures 1a–1d). Convection sharpens the MEG-water interface (Figure 1e), and the motion of the interface provides a clear and direct measure of the convective flux  $F_c = \phi v_i \Delta$  as a function of the interfacial velocity  $v_i$ , the porosity  $\phi$  and the concentration difference between pure MEG and water,  $\Delta$ . In all experiments the interface recedes at a constant speed, independent of the plume position, indicating a constant convective flux which depends only on the Rayleigh number,

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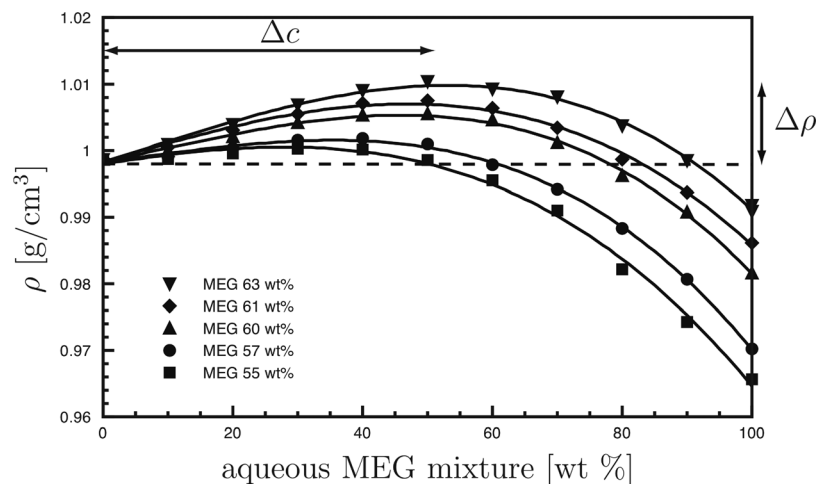
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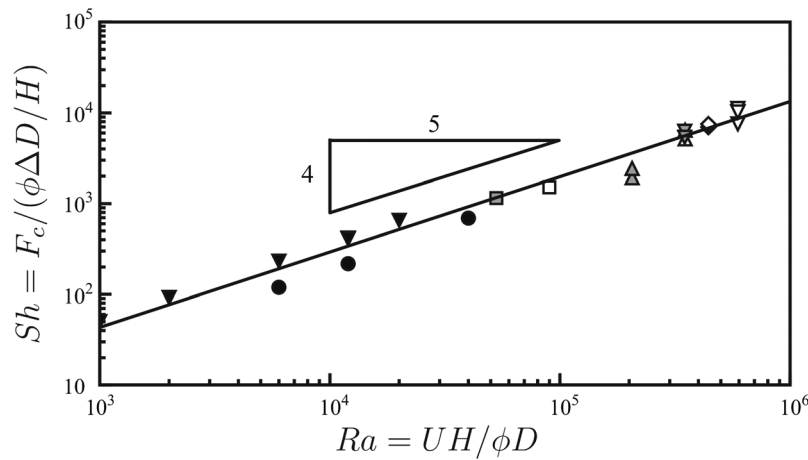
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**Figure 1.** Snapshots of the (a–e) experimental and (f–i) numerical results for the dissolution of  $\text{CO}_2/\text{MEG}$  in a water saturated porous medium. The unprocessed experimental image (shown in Figure 1a) shows the mixing of a MEG solution with 63 wt% ethylene-glycol (blue) in a porous medium of size  $1.4 \times 40 \times 80$  cm (black bar shown for scale in Figure 1a is 5 cm) with a Rayleigh number of  $Ra = 5.9 \times 10^5$ . The dye intensity allows a corresponding map of concentration to be produced (Figure 1b). Figures 1b–1d show concentration maps taken at  $t = 10, 40$  and  $70$  minutes. Horizontal averages of these concentration maps produce the width-averaged concentration profiles (Figure 1e) at times  $t = 10$  (blue),  $40$  (red) and  $70$  minutes (black). Concentration maps taken from a numerical simulation with  $Ra = 2 \times 10^4$  are shown in Figures 1f–1h. The width-averaged concentration profiles shown in Figure 1i are plotted at  $t = 3.1$  (blue),  $6.4$  (red) and  $9.6$  (black). The width-averaged experimental and numerical profiles allow a quantitative measure of the interface velocity and hence the convective flux.



**Figure 2.** The density of methanol and ethylene-glycol (MEG) mixed with water, for MEG solutions with different wt% ethylene-glycol. The maximum density difference between MEG and water is given by  $\Delta\rho$ , at concentration  $\Delta c$ .

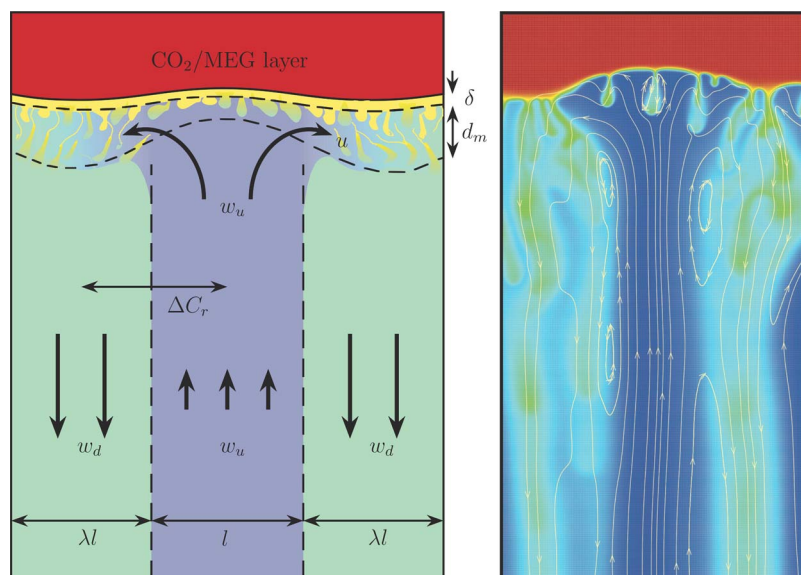


**Figure 3.** The Sherwood number  $Sh$ , a dimensionless measure of the convective flux, is shown as function of Rayleigh number,  $Ra$ . The results from high-resolution numerical simulations are shown in black. Experimental measurements for porous media of permeability  $k = 1.4 \times 10^{-5} \text{ cm}^2$  are shown shaded grey and with permeability  $k = 2.4 \times 10^{-5} \text{ cm}^2$  are clear. The MEG concentration is indicated by the symbols used in the legend of Figure 1.

$Ra = UH/\phi D$ , where  $H$  is the depth of the reservoir,  $D$  the diffusivity and  $U = kg\Delta\rho/\mu$  the natural Darcy buoyancy flux, defined in terms of the permeability  $k$ , maximum density difference  $\Delta\rho$  (Figure 2), gravitational acceleration  $g$  and viscosity  $\mu$ . A series of high-resolution numerical simulations of this system confirm the experimental results and extend them to lower  $Ra$ . The combined data set (Figure 3) shows that the dimensionless flux, given by the Sherwood number  $Sh = F_c/(\phi\Delta D/H)$ , follows the power law relationship  $Sh = bRa^n$  with  $b = 0.12 \pm 0.03$  and  $n = 0.84 \pm 0.02$ . We see that the compositional flux in penetrative high Rayleigh number convection is reduced from the classical linear scaling,  $Ra \propto Sh$ . This linear scaling results from the assertion that the flux is independent of the depth  $H$  and is therefore determined solely by the stability of a thin diffusive boundary

layer at the interface [Howard, 1964]. In contrast, at high Rayleigh number, nonlinear scaling relationships have been observed in thermal porous convection [Elder, 1967; Otero *et al.*, 2004], and analogous regimes are found in high Rayleigh number free-fluid convection [Castaing *et al.*, 1989]. The physical origins of this regime have remained unexplored for porous convection.

[5] The numerical and experimental results suggest a physical picture that captures the dynamics in three regions: a diffuse boundary layer at the interface between  $\text{CO}_2$  (or MEG) and water becomes unstable to saturated fingers which are born, swept aside and coalesce in a mixing region before descending into the far field as long-lived plumes (shown schematically in Figure 4). Lateral compositional diffusion from descending plumes into the upwelling flows therefore



**Figure 4.** (a) A sketch of the dynamical regimes outlined in the scaling argument alongside (b) an image from the numerical calculations showing concentration contours and streamlines. The scaling models a far-field that is dominated by plumes of width  $\lambda l$  that originate within a mixed region of width  $d_m$  in which instabilities grow from a boundary layer of width  $\delta$ .

acts to reduce the density difference driving the descending plumes. The compositional flux is reduced relative to the classical limit.

[6] Far from the interface, long-lived plumes descend at a velocity set by the density contrast between upwelling and descending plumes which is proportional to the reduced concentration difference  $\Delta c_r$ . Lateral diffusion between enriched downwelling and relatively fresh upwelling plumes reduces the concentration difference from the classical limit,  $\Delta c_r < \Delta c$ , and results in a reduced downwelling velocity  $w_d \sim U\Delta c_r/\Delta c$ . In this region fluid flow is predominantly vertical. Hence mass conservation implies that upwelling plumes of width  $l$  pass downwelling plumes of width  $\lambda l$  with velocity  $w_u \sim \lambda w_d$ . A balance exists within the long-lived plumes between vertical advection and lateral diffusion,

$$w_u \frac{\partial c}{\partial z} \sim D \frac{\partial^2 c}{\partial x^2},$$

so  $\lambda w_d \Delta c/H \sim D\Delta c_r/l^2$ . As the upwelling fluid approaches the interface it is forced laterally and behaves much like a stagnation point flow [Batchelor, 1967] with comparable lateral and vertical velocities  $u \sim w_u$ . Within this mixing region, whose depth is comparable to the lateral spacing of the downwelling plumes,  $d_m \sim \lambda l$ , advection dominates,

$$u \frac{\partial c}{\partial x} + w_u \frac{\partial c}{\partial z} \sim 0,$$

and so the areal concentration of descending plumes is related to the vertical ( $\Delta c$ ) and horizontal ( $\Delta c_r$ ) concentration gradients by  $\lambda \sim (\Delta c_r/\Delta c)^{-1}$ . We now assume a power law dependence of the concentration gradients on the Rayleigh number,  $\Delta c_r/\Delta c \equiv Ra^\gamma$ , where  $\gamma$  is determined by the scaling analysis and the requirement of mass conservation between regions.

[7] Flow within the mixing region acts to stabilize the diffusive boundary layer, which therefore has the characteristic thickness of a diffusive field in a stagnation point flow,  $\delta \sim (Dl/u)^{1/2}$ . The compositional flux through the diffusive boundary layer must match the flux through the mixing region, and be equal to the advective flux within the descending plumes. The balance of fluxes,  $ID\Delta c/\delta \sim \lambda l w_d \Delta c_r$ , therefore constrains the width of the downwelling plumes. The flux across the boundary layer, and therefore through the entire system, is given by  $F_c = F_{bl} \sim \phi D\Delta c/\delta$ . The reduced density difference, which drives the descent of plumes, is predicted by our scaling analysis to be  $\Delta c_r/\Delta c \sim Ra^{-1/5}$ . This reduction in the density contrast, in combination with the effect of flow on the diffuse boundary layer, produces a nonlinear scaling for the convective flux  $Sh = \alpha Ra^{4/5}$ , where our experimental and numerical data suggests that  $\alpha = 0.19 \pm 0.01$ .

[8] We can now estimate the mass flux of dissolved CO<sub>2</sub> in an idealised sequestration site. Sample calculations are performed for a relatively porous,  $\phi = 0.375$ , and permeable,  $k = 2.5 \times 10^{-12} \text{ m}^2$  (assumed isotropic), sandstone interbedded by impermeable horizontal shale layers,  $H \sim 20 \text{ m}$ , motivated by the Sleipner site in the North sea [Bickle et al., 2007]. We take conditions at a depth of 1 kilometer to be  $\Delta\rho = 10.5 \text{ kg m}^{-3}$ ,  $\mu = 5.9 \times 10^{-4} \text{ Pa s}$  and  $D = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  [Pau et al., 2010], and therefore the Rayleigh number is large,  $Ra \sim 1.2 \times 10^4$ . Convective dissolution is therefore expected

to play an important role in the long-term fate of stored CO<sub>2</sub>, giving rise to a convective flux of

$$F_{CO_2} = \frac{\phi D \Delta_{CO_2}}{H} Sh = \alpha \Delta_{CO_2} \left( \frac{\text{kg} \Delta \rho}{\mu} \right)^{4/5} \left( \frac{\phi D}{H} \right)^{1/5} \\ \simeq 20 \text{ kg m}^{-2} \text{ yr}^{-1}$$

into the ambient brine, where  $\Delta_{CO_2}$  is the mass fraction of CO<sub>2</sub> in the saturated brine. To place this figure in context, the areal extent of the CO<sub>2</sub> plume at Sleipner in 2002 was approximately  $A \sim 5.6 \times 10^6 \text{ m}^2$  as inferred from seismic images. In our model calculation convective dissolution would account for a flux of  $10^8 \text{ kg CO}_2 \text{ yr}^{-1}$ , or roughly 10% of the annually injected mass, from the spreading plumes. In many sequestration sites, the multiphase spreading of CO<sub>2</sub> plumes increases the interfacial area and enhances convective dissolution. Convective dissolution limits the maximum extent of the CO<sub>2</sub> plume and will reduce the extent of the plume in the long term. This sample calculation shows that trapping through convective dissolution is an important physical process that can reduce the risk of leakage in geological storage sites.

[9] Natural CO<sub>2</sub> accumulations provide a window through which to view the deep carbon cycle, and valuable analogues for the long term evolution of geological CO<sub>2</sub> storage. Such natural accumulations occur in a variety of geological settings and are thought to have existed over  $10^4$  to  $10^6$  years. Even a reduced convective flux, due to low permeability, would provide for the dissolution of large quantities of CO<sub>2</sub>. This raises a series of fundamental questions about the deep carbon cycle as well as our understanding of convection in natural systems. How is convective dissolution affected by mixing during emplacement of CO<sub>2</sub> and the buildup of CO<sub>2</sub>-saturated waters within deep aquifers, and over what time scale will these reservoirs reach their final state. Convective dissolution may cease in some closed reservoirs due to saturation of the brine with CO<sub>2</sub>. However, many natural accumulations occur in large regional aquifers with tilted gas-water contacts indicating active background flow that are unlikely to saturate and will interact extensively with the surrounding hydrologic system over long periods of time. To answer these questions, a new interdisciplinary research effort on the dynamics of natural CO<sub>2</sub> reservoirs is required that relates geochemical observations to dynamic models of multiphase flow.

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